AD-A199 681 SURFACE DYNAMICS OF RARE GAS CRYSTALS(U) CHICAGO UNIV IL JAMES FRANCK INST K D GIBSON ET AL. AUG 85 TR-5 N00014-77-C-0240 1/1

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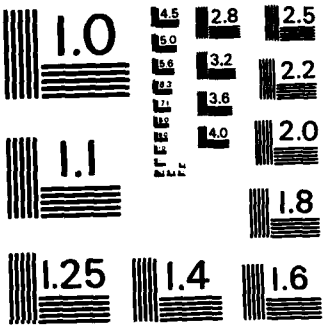

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: 5	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): SURFACE DYNAMICS OF RARE GAS CRYSTALS		5. TYPE OF REPORT & PERIOD COVERED: Interim Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): K. D. Gibson and S. J. Sibener		8. CONTRACT OR GRANT NUMBER(s): N00014-77-C-0240
9. PERFORMING ORGANIZATION NAME AND ADDRESS: The University of Chicago, The James Franck Institute, 5640 South Ellis Avenue, Chicago, IL 60637		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR-392-023
11. CONTROLLING OFFICE NAME AND ADDRESS: The Office of Naval Research, Physical Sciences Division (Code 421), 800 North Quincy Str., Arlington, VA 22217		12. REPORT DATE: August, 1985 13. NUMBER OF PAGES: 9
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report): unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

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18. SUPPLEMENTARY NOTES
Prepared for Publication in Journal of Vacuum Science and Technology.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Surface phonon spectroscopy; phonon dispersion curves; surface dynamics; thin films; inelastic single phonon scattering; physisorption interactions; gas-surface energy exchange; rare gas interaction potentials.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The surface properties of rare gas crystals have been explored using a He molecular beam as the dynamical probe. Specifically, ordered monolayer, bilayer, trilayer, and bulk Ar, Kr, and Xe were grown on an Ag(111) substrate. This has allowed us to examine how the physical properties of these films evolve on a layer by layer basis. Elastic diffraction and selective adsorption experiments were used to investigate the He-surface interaction potential. Comparing the results of close-coupled calculations with the experimental data, both the laterally averaged potential and higher order terms in the energy expansion can

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be determined. To examine the dynamical properties of the adsorbed rare gases, angle and time resolved inelastic scattering was used. This technique made it possible to investigate the dynamics of the surface across the entire Brillouin zone. In this paper the properties of Ar(111) multilayers are specifically examined. These data are compared to the theoretical calculations of several other groups, testing the validity of several model potentials, and the importance of various interaction terms when constructing these potentials.

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Surface Dynamics of Rare Gas Crystals

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PACS: 79.20.Rf; 63.20.Dj; 68.30.+z; 68.60.+q

ABSTRACT

The surface properties of rare gas crystals have been explored using a He molecular beam as the dynamical probe. Specifically, ordered monolayer, bilayer, trilayer, and bulk Ar, Kr, and Xe were grown on an Ag(111) substrate. This has allowed us to examine how the physical properties of these films evolve on a layer by layer basis. Elastic diffraction and selective adsorption experiments were used to investigate the He-surface interaction potential. Comparing the results of close-coupled calculations with the experimental data, both the laterally averaged potential and higher order terms in the energy expansion can be determined. To examine the dynamical properties of the adsorbed rare gases, angle and time resolved inelastic scattering was used. This technique made it possible to investigate the dynamics of the surface across the entire Brillouin zone. In this paper the properties of Ar(111) multilayers are specifically examined. These data are compared to the theoretical calculations of several other groups, testing the validity of several model potentials, and the importance of various interaction terms when constructing these potentials.

Originator Supplied Keywords Included

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In this paper we present preliminary results dealing with the surface dynamics of ordered rare gas overlayers physisorbed on an Ag(111) substrate. The overlayers examined were 1, 2, 3, and 25 layer (111) oriented films of Ar, Kr, and Xe. Experiments with physisorbed rare gas films on other metal surfaces have been reported by Mason and Williams [1]. However, in this paper we report for the first time, to our knowledge, how the surface phonon relations evolve on a layer-by-layer basis from monolayer to bulk across the Brillouin zone. Our experimental results were obtained using the angle resolved time of flight (TOF) of inelastically scattered He. Inelastic He scattering is a good technique for probing these weakly bound systems because of its surface sensitivity, excellent energy resolution ($\sim$250μeV), and because the momentum of the incident beam is of the right order of magnitude to probe the entire Brillouin zone for the low energy modes of these materials. A complete description of the experimental procedure and apparatus will appear in forthcoming publications [2].

Thermodynamic and structural information for rare gas overlayers on Ag(111) was already available from LEED experiments [3,4] and theoretical calculations [5]. These form hexagonal structures that are azimuthally aligned but incommensurate with the surface. Overlayers were grown on a cryogenically cooled Ag(111) crystal with a low pressure dosing beam by controlling the crystal temperature, beam pressure, and dosing time. The ordering and lattice constants were checked using elastic He diffraction. The angular profiles obtained in these diffraction runs indicate that the coherence lengths of these overlayers are only slightly less than that of the Ag substrate ($\sim$100 Å). When an experiment on a particular overlayer was completed, the number of layers was confirmed by temperature programmed thermal desorption. By controlling the rate of the temperature ramp, the

monolayer desorption peak occurred separately from any of the multilayer peaks. Therefore, the coverage could be quantitatively determined by comparing the total integrated signal to that of the monolayer.

The data were analyzed by first fitting the TOF peaks with a nonlinear least squares routine. Examples of the data and the fits are shown in Figure 1. The arrow indicates the TOF of elastically scattered He. In general, there was always a peak at this position, which we attribute to incoherent scattering from crystal defects. The well resolved peaks show that with an 18 meV incident beam, single phonon events are the predominant inelastic scattering channel. To give an idea of the probabilities for inelastic scattering, the large energy loss peak of the monolayer has an intensity which is $\sim 1 \times 10^{-3}$ of the specular beam, and $\sim 1 \times 10^{-5}$ of the incident beam. The intensity of the principal modes observed do not vary by more than a factor of five from zone center to edge ($\bar{\Gamma} \rightarrow \bar{M}$). The difference in the flight times for these peaks compared with the elastic TOF (determined at the specular angle) was used to determine the phonon energies. Using this information, and the incident and detector angles, the momentum exchange with the surface was calculated. Most of the experiments were done at an incident angle of 45 degrees, and the Brillouin zone was probed by varying the detector angle.

Figure 2 is a reduced zone plot of the dispersion relations for Ar in the $\bar{\Gamma} \rightarrow \bar{M}$ direction. This figure clearly shows that inelastic He scattering experiments can be used to quantitatively probe how the surface vibrations of thin films evolve, on a layer-by-layer basis, from monolayer to bulk. This also indicates how the forces present at the surfaces of thin supported films vary with increasing distance of the surface from the substrate. The same qualitative features have also been seen for Kr and Xe.

The monolayer $SP_{\perp}$ mode (the only monolayer mode observed) is found to be dispersionless within experimental error. This indicates that the adsorbed atoms are behaving as independent Einstein oscillators, moving in an uncorrelated fashion in the surface potential well. Only the single phonon inelastic events corresponding to the energy loss and gain peaks adjacent to the elastic position in Figure 1 are plotted in Figure 2. This monolayer frequency gives the curvature at the equilibrium position, an essential piece of information for constructing the interaction potential. Temperature dependent studies show that the relative intensities of the single phonon creation and annihilation peaks vary in a manner consistent with statistical expectations. There are also two other peaks in the monolayer spectrum of Figure 1, corresponding to phonon creation, with energies twice and three times the fundamental. Due to the nearly harmonic nature of the rare gas-surface holding potential, we are at this time unable to determine the relative importance of overtone and multiphonon excitations in explaining these energy loss features. As further overlayers are added, the amount of dispersion increases as lateral interactions become systematically more important. Again, note that only the energy gain and loss features immediately adjacent to the elastic time of flight in Figure 1 were used in constructing the multilayer dispersion curves shown in Figure 2.

Lattice dynamics calculations have been carried out which well represent our experimental dispersion curves [6]. These calculations demonstrate the adequacy of using known gas phase pair potentials for modelling the interactions present in condensed rare gas films, and the importance of the substrate in modifying the phonon frequencies. Work is currently in progress to determine the inelastic scattering probabilities from the TOF spectra.

Acknowledgments: We would like to thank B. Hall, D. Mills, J. Black, M. Klein, and L. Bruch for their theoretical assistance. This work was supported in part by the ONR and the NSF-MRL at The University of Chicago. S. J. Sibener also acknowledges support from a Camille and Henry Dreyfus Foundation Young Faculty Grant.

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Figure Captions

Figure 1 TOF spectra of the Ar overlayers studied at a surface temperature of 12 K and an incident beam energy of 18 meV. Crosses are the experimental data, solid lines are a least-squares fit of these data, and dashed lines are a computer simulation assuming single phonon processes and delta function phonon energy widths. Arrows indicate position of elastic incoherent scattering. The spectra were collected for 1 hour with 1 usec/channel resolution at an incident angle of 45 degrees. The detector angle was, from top to bottom, 42, 39, 40, and 50 degrees.

Figure 2 Dispersion curves of the Ar overlayers from $\bar{\Gamma}\rightarrow\bar{M}$. Open symbols are for energy loss of the beam, closed symbols are for energy gain. Representative error bars are shown for energy and momentum loss features (with respect to the He beam) which occurred in the first zone. Solid lines are polynomial fits to the data.

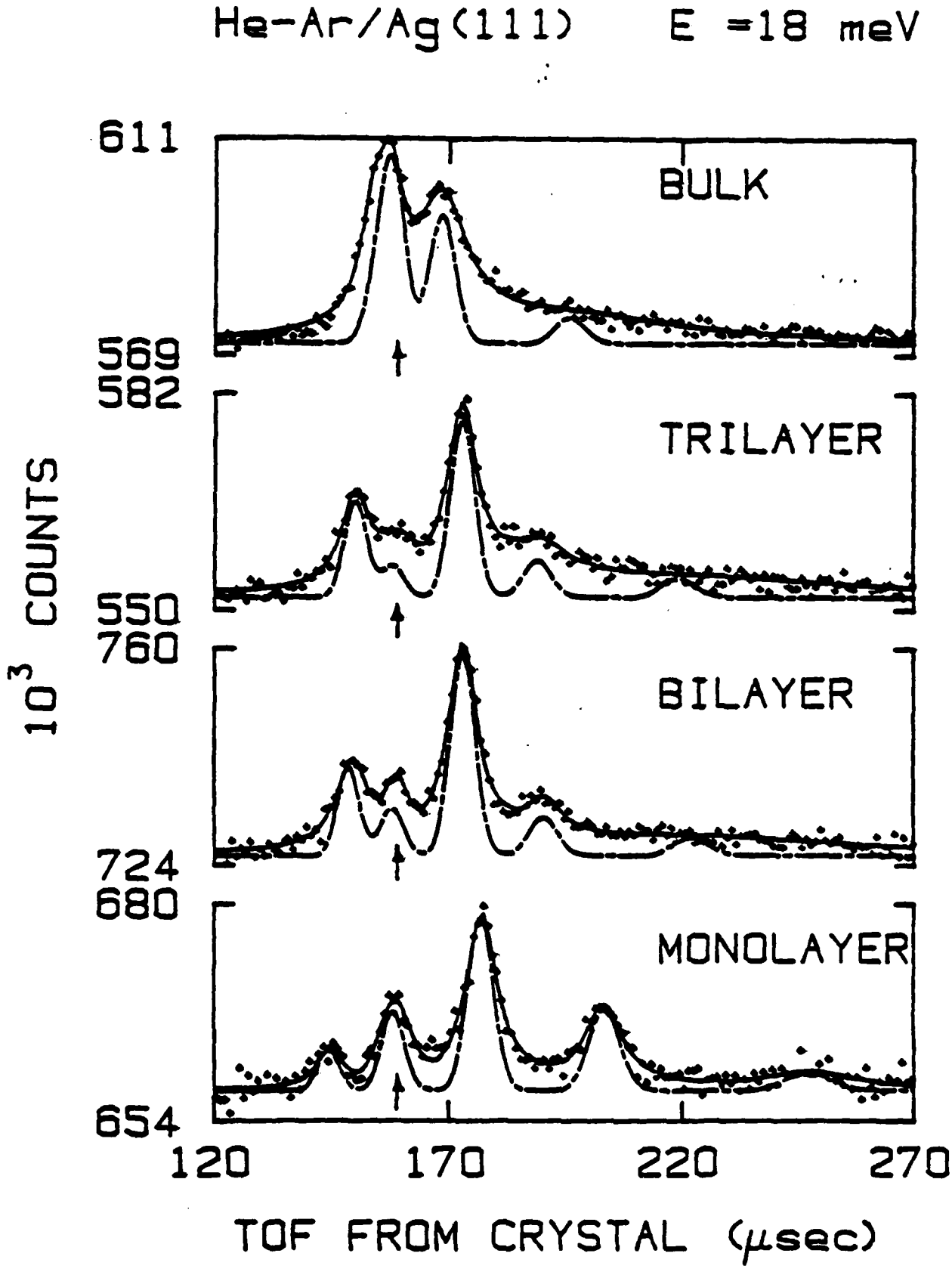
He-Ar/Ag(111) E =18 meV
611
569
BULK
582
550
TRILAYER
760
724
BILAYER
680
654
MONOLAYER
10^3 COUNTS
120
170
220
270
TOF FROM CRYSTAL (μsec)

FIGURE 1

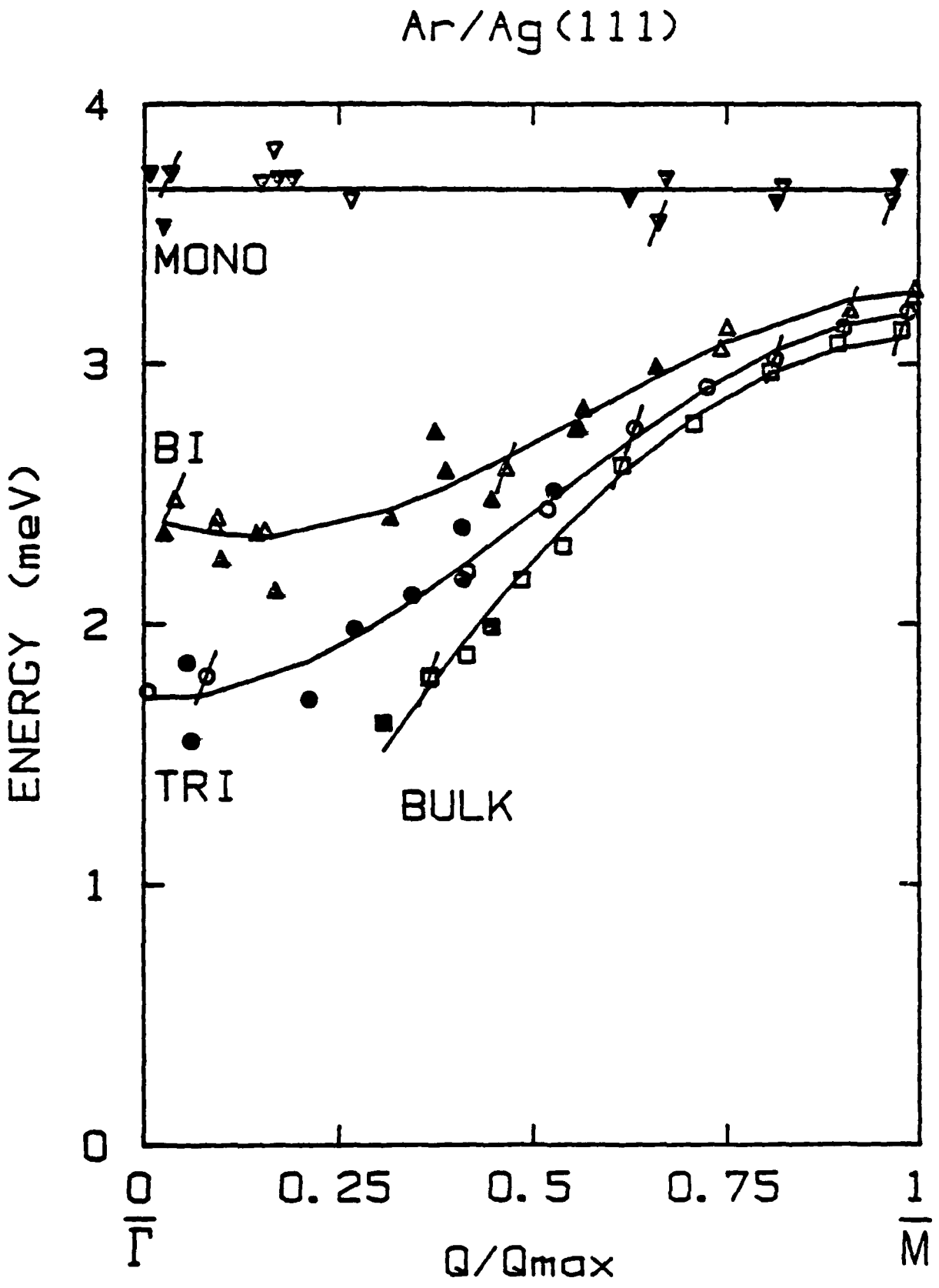
Ar/Ag(111)
ENERGY (meV)
4
3
2
1
0
MONO
BI
TRI
BULK
0
Γ
0.25
0.5
0.75
1
M
Q/Qmax

FIGURE 2

END

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